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APPLICATION NUMBER: 60/506,286
FILING DATE: *September 26, 2003*

Certified by



Jon W Dudas

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EV299956996US

17958 U.S. PTO
 60/506286
 09/26/03

Given Name (first and middle [if any])		INVENTOR(S)		Residence (City and either State or Foreign Country)	
LAMBERTUS GERHARDUS JOHANNUS LUDWIG		Family Name or Surname OLDE HANTER EISENHUTH		WEERSELO, NETHERLANDS OBERNBURG, GERMANY	
Additional inventors are being named on the _____ 2nd _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max) Process for Enhancing the Melt Strength of Polypropylene					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input type="checkbox"/> Customer Number: _____ OR <input checked="" type="checkbox"/> Firm or Individual Name: LOUIS A. MORRIS Address: AKZO NOBEL INC. Address: 7 LIVINGSTONE AVENUE City: DOBBS FERRY Country: UNITED STATES OF AMERICA State: NY Zip: 10522-3408 Telephone: (312) _____ Fax: (312) 544-7379					
ENCLOSED APPLICATION PARTS (check all that apply) 544-7378					
<input checked="" type="checkbox"/> Specification Number of Pages 11 <input type="checkbox"/> Drawing(s) Number of Sheets _____ <input type="checkbox"/> Application Date Sheet. See 37 CFR 1.76 <input type="checkbox"/> CD(s), Number _____ <input type="checkbox"/> Other (specify) _____					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. <input type="checkbox"/> A check or money order is enclosed to cover the filing fees. <input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 01-1350 <input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
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<input checked="" type="checkbox"/> No. <input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,

[Page 1 of 2]

SIGNATURE

Date SEPTEMBER 26, 2003

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REGISTRATION NO. 30,697

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(if appropriate)
 Docket Number: AFL3017PRUS

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INVENTOR(S)					
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)			
ARIE JACOB	DE HOOG	UGCHELEN, NETHERLANDS			
Additional inventors are being named on the _____ separately numbered sheets attached hereto					
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Page Two of Two

Respectfully submitted,

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PROCESS FOR ENHANCING THE MELT STRENGTH OF POLYPROPYLENE

The invention relates to a process for enhancing the melt strength of polypropylene (PP), to a composition for said process, to polypropylene with enhanced melt strength, and to the use of said composition of polypropylene for making an article.

5

Processes for enhancing the melt strength of PP are known. For instance in WO 99/27007 PP is mixed with at least a peroxydicarbonate to give PP with enhanced melt strength. This method has the disadvantage that peroxide compounds are required. Peroxides generally unfavorably affect the molecular weight of the starting PP by cleaving the polymer chains. Furthermore, the use of peroxides is hampered by serious safety risks, particularly by the explosion risk. Other references using peroxide initiators are EP 907677 and JP 60055012. The latter reference, moreover, discloses an adhesive compound further comprising a hydroxy group-containing organic compound, whereas no enhanced melt strengths are reported.

15

In US 2003/0092816 enhanced melt strength is obtained by making a PP composition with smectic clay that has been ion-exchanged and intercalated with a quaternary ammonium compound and a PP grafted with an ethylenically unsaturated carboxylic acid. Such compositions with modified clays and grafted polymers are not always optimal for any application.

20

To alleviate the above disadvantages there is a need for a simple extrusion process for making PP with enhanced melt strength, which is free, or at least substantially free, from peroxides and also from hydroxy group-containing organic compounds.

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To this end, the present invention provides a process for enhancing the melt strength of polypropylene comprising the steps of:

-mixing 100 parts per weight (ppw) of the polypropylene with at least 0.1-8 ppw of an oligomer of maleimide or a derivative thereof, completely or substantially in the absence of peroxide;

5 -reacting said polypropylene and oligomer of maleimide or a derivative thereof at a temperature between 150° C and 300° C.

The terms "substantially free" and "substantially in the absence" mean that less than 0.01 ppw of the indicated component is present in the composition. Preferably, such components are totally absent.

10

In another embodiment of this invention the process for enhancing the melt strength of polypropylene comprising a step wherein the oligomer of maleimide or a derivative thereof is prepared *in situ* by mixing the polypropylene with maleimide monomer or a derivative thereof and a base.

15

The term "polypropylene" (PP) refers to polymers or mixtures of polymers containing at least 50 % by weight of polymerized propylene. Polymerization catalysts may be Ziegler-Natta, metallocene, or other types giving stereospecific polymerization of propylene. Use may be made in this connection of
20 homopolymers of propylene; random, alternating, or block copolymers; or random, alternating, or block terpolymers of propylene and another olefin. Generally, a propylene copolymer or terpolymer will contain one or more other olefins, such as ethylene, butene, pentene, hexene, heptene, or octene, but it may also comprise other olefinically unsaturated monomers or combinations of
25 these, such as acrylates, styrene, styrene derivatives, acrylonitrile, vinyl acetate, vinylidene chloride, and vinyl chloride.

It is preferred here to restrict the content of olefins other than propylene to 30 % by weight of the copolymer. Especially suited are homopolymers of propylene,

copolymers of propylene and ethylene or mixtures of polypropylene and polyethylene containing not more than 10 % by weight of polymerized ethylene.

5 The melting point of normally solid commercially available PP is about 160-170° C. The melting point of propylene copolymers and tercopolymers in general can be lower. The process of the invention preferably is carried out at a temperature in the range of from 150 to 300° C, more preferably from 160 to 250° C., and most preferably from 170 to 225° C.

10 The molecular weight of the PP used can be selected from a wide range. Indicative of the molecular weight is the melt flow index (MFI). Use may be made of a PP having a MFI from 0.1 to 1000 g/10 min (230° C, 21.6 N). Preferably, use is made of a PP having a MFI from 0.5 to 250 g/10 min.

15 The process according to the present invention is suitably carried out in melt mixing equipment known to a person skilled in the art. Preferably, an extruder or a kneader is used. More preferably, use is made of a single or twin-screw extruder. An internal mixer such as a Banbury mixer optionally coupled to an extruder may also be used.

20 The term "maleimide (derivative)" as herein used include maleimide, maleimide derivatives, and oligomers thereof. The maleimide (derivative) may be mixed first with the PP and then the mixture may be extruded. Alternatively, the maleimide (derivative) may be added to the extruder already containing the PP
25 by injection or spraying, or may be added together with the PP. This is especially preferred when oligomers are used. When monomers are used the maleimide (derivative) is added together with the base. It is preferred to introduce a solid or semi-solid maleimide (derivative) together with the PP into the extruder, for example, by using a feeder. The temperature setting of the extruder should allow
30 the PP to melt, i.e. above 150° C. The screw speed typically is from about 25 to

500 rpm. According to the invention the preferred maleimide (derivative) is derived from biscitraconic acid or the oligomer thereof. The quantity of maleimide (derivative) is 0.1-8 ppw per 100 ppw of PP. Preferably, the quantity of maleimide (derivative) is 1-4 ppw.

5

The base may be any base that is known in the art. Particularly useful bases are tertiary amino bases, such as 1,4-diazabicyclo[2,2,2]octane, which is commercially known as Dabco®, imidazole, guanidine and derivative thereof, inorganic bases such as sodium hydroxide, and trialkylamines. Practical

10

Normal residence time in the extruder is 15 sec to 30 min. The longer residence times can be achieved by using additional static mixers, and the like.

15

The extruded strand may be further processed as known to one of ordinary skill in the art. Normally, the extruded strand is fed through a water bath and granulated using a granulator. Alternatively, the extruded modified PP is formed directly into a desired end product.

20

It is preferred to carry out the process of the present invention in an atmosphere of an inert gas, such as nitrogen or argon. Preferably, nitrogen is used.

25

Solid as well as liquid maleimide (derivative) may be used in the process according to the present invention. A solution of a maleimide (derivative) in an inert solvent, such as isododecane, or in the form of frozen flakes, may also be used. Suitable inert solvents are known to one skilled in the art. It is preferred to use a solid maleimide (derivative) in the form of, for example, flakes, finely divided particles (powder), or a liquid maleimide (derivative).

30

Optionally, the modified PP may be purified, modified, or molded in one or more process steps, prior to its final processing. Thus, there may be further

modification using another polymer or monomer in order to enhance the end product's compatibility with other materials. Alternatively, the modified PP may be degraded or, on the contrary, cross-linked slightly, to increase its processability and/or applicability. The modified PP according to the invention has a melt strength that is at least 1.5, preferably 1.8 times higher than the melt strength of the starting not-modified PP. Generally, to achieve the desired end conventional adjuvants in an amount known to one skilled in the art, such as antioxidants, UV-stabilizers, lubricants, antidegradants, foaming agents, nucleating agents, fillers, pigments and/or antistatic agents are added to the PP. These adjuvants can be added to the PP before as well as during or after the modifying step according to the invention. For example, a blowing agent can be added or gas can be injected into the extruder before, during or after the modification, in order to produce foamed PP.

The PP obtained by the invention process does not show a substantial difference in weight average molecular weight, indicating that cleavage of the polymer chain does not occur. Only oligomers of maleimide (derivative) or mixtures thereof (or their precursors, i.e., mixtures of maleimide (derivative) monomers with bases) have been found to give the desired enhanced melt strength in the process of the present invention. Oligomers of maleimide (derivative) or mixtures thereof can for instance be prepared by anionic or radical polymerization of maleimide (derivatives). It was found that such oligomers could be directly added tot the PP in the melt phase, or that such oligomers could *in situ* be prepared by the addition of maleimide (derivative) monomers in the presence of a base to the PP, without leading to modified polypropylenes of significant different melt strength.

The PP obtained using the process according to the present invention may be processed into an end product without any further adaptations if so desired. The modified PP can be processed into the desired end product, such as foams, fibers, or sheets in all kinds of ways known to the skilled person, with the

processing conditions generally being dependent on the material and equipment employed, such as, for example, by foaming, foam molding, extrusion, injection molding, blow molding, extrusion coating, profile extrusion, or thermoforming.

5 The invention is illustrated by the following Examples.

The following materials and methods are employed in the Examples:

Polypropylene: PP HC001A-B1, ex Borealis, Austria

Perkalink® 900: meta-xylylene biscitraconimide ex Flexsys, USA

Dabco®: 1,4-diazabicyclo[2,2,2]octane, ex Tosoh, Japan

10

PROCEDURE A

Mixing procedure:

The maleimide compound Perkalink® 900 and Dabco® were added to polypropylene powder in a bucket and tumble-mixed by hand for 5 minutes at room temperature. Compounds were extruded immediately after mixing.

15

Compounding procedure:

All compounds were melt-modified by extrusion in a Haake "TW100" twin screw extruder with intensive mixing screws attached to a Haake "Rheocord System 40". During the experiment nitrogen was passed in counterflow from the hopper up through the feeder.

20

The extruder comprised a barrel housing four consecutive temperature chambers, wherein the first chamber had a temperature of 180° C, the second 180° C, the third 180° C, and the fourth chamber 190° C. The screw speed was 80 rpm. The extruded strand was fed through a water bath and granulated with an Automatic "ASG5" granulator.

25

Test procedures:

MFI (Melt Flow Index), characterizing the flow behavior of a PP melt, was measured with a Goettfert Melt Indexer (model MP-D) according to DIN 53735

30

and ASTM 1238 (230° C, 21.6 N load).

Melt strength, i.e. the ability of a melt of PP to withstand a tensile elongation or stretching without breaking, was measured using one of two instruments:

- Instrument 1: a Goettfert Rheotens attached to a Goettfert Rheograph 2001 capillary rheometer (200° C, die geometry 30/1mm, initial speed 20 mm/s, acceleration 1.2 mm/s², strand length 100 mm).

-Instrument 2: a Goettfert 71.97 (200°C, die geometry 30/2mm, initial speed 18.5mm/s, acceleration 30 mm/s², strand length 100mm).

Example 1:

1000 g of polypropylene powder were mixed with 30 g of Perkalink® 900 and 2 g of Dabco® as described above. The mixture was melt extruded in a Haake "TW100" twin screw extruder under the conditions given above.

The obtained product had a MFI of 2.2 g/10 min and a melt strength of 42 cN (200° C, acceleration 30 mm/s²). In comparison the non-modified polypropylene used has an MFI of 7.6 g/10 min and a melt strength of 22 cN (measured on Instrument 2).

Example 2:

Example 1 was repeated, but 20 g of Perkalink® 900 and 5 g of Dabco® were used.

The product had a melt flow of 2.1 g/10 min and a melt strength of 40 cN (measured on Instrument 2).

Example 3:

40 g of Perkalink® 900 and 8 g of Dabco® were dissolved in 200 ml of toluene and refluxed for 1 h. The toluene was removed and a mixture of oligomers was obtained wherein part of the C-C double bonds of the Perkalink® 900 was changed by reaction (according to NMR analysis). 30 g of the thus obtained

product were mixed with polypropylene powder as described above and melt extruded as in Example 1.

The product was clear but slightly brownish and had an MFI of 2.1 g/10 min and a melt strength of 42 cN (measured on Instrument 1).

5

Example 4:

Example 1 was repeated, but 50 g of Perkalink® 900 were used.

The product had a MFI of 2.3 g/10 min and a melt strength of 13.5 cN (measured on Instrument 1). The not modified PP used had a MFI of 7.6 g/10 min and a melt strength of 3.4 cN.

10

Example 5:

Example 1 was repeated, but 30 g of meta-phenylene bismaleimide were used instead of Perkalink® 900, and no Dabco® was used.

The modified PP made in this way had a MFI of 0.9 g/10 min and a melt strength of 11 cN (measured on Instrument 1).

CLAIMS

1. A process for enhancing the melt strength of polypropylene comprising the steps of:
 - mixing 100 parts per weight (ppw) of the polypropylene with at least 0.1-8 ppw of an oligomer of maleimide or a derivative thereof, completely or substantially in the absence of peroxide;
 - reacting said polypropylene and oligomer of maleimide or a derivative thereof at a temperature between 150° C and 300° C.
2. The process according to claim 1 wherein the oligomer of maleimide or a derivative thereof is prepared *in situ* by mixing the polypropylene with maleimide monomer or a derivative thereof and a base.
3. The process according to claim 1 wherein the maleimide derivative oligomer is derived from biscitraconic acid.
4. The process according to claim 2 wherein the maleimide derivative is derived from biscitraconic acid and the base is 1,4-diazabicyclo[2,2,2]octane.
5. A composition, which is completely or substantially free from peroxide, comprising 100 ppw of polypropylene and 0.1-8 ppw of an oligomer of maleimide or a derivative thereof, or a mixture of 0.1-8 ppw of a monomer of maleimide or a derivative thereof and a base.
6. The composition of claim 5 wherein the maleimide derivative is derived from biscitraconic acid and the base is 1,4-diazabicyclo[2,2,2]octane.
7. A completely or substantially peroxide free polypropylene obtainable from the composition of claim 5 or 6 with enhanced melt strength,

which is at least 1.5 times higher than the melt strength of the corresponding non-modified polypropylene.

- 5 8. Use of the composition of claim 5 or 6 or of the polypropylene of claim 7 for making a foam, fiber, or sheet.

Abstract

The invention relates to a process for enhancing the melt strength of polypropylene comprising the steps of:

- mixing 100 parts per weight (ppw) of the polypropylene with at least 0.1-8 ppw of an oligomer of maleimide or a derivative thereof, completely or substantially in the absence of peroxide;
- reacting said polypropylene and oligomer of maleimide or a derivative thereof at a temperature between 150° C and 300° C.

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